Understanding the structure-reactivity relationship of Mn oxides toward contaminant sequestration

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Manganese oxides (MnOx) are a group of ubiqitous metal oxides with great environmental significance. Due to their small particle size, large surface area, and high sorptive and oxidative capacities, MnOx can participate in a wide range of sorption and redox reactions, and exert significant influences on the biogeochemical cycling of metals, nutrients, and organics. The majority of natural MnOx are thought to be formed from microbial activities and the predominant form of biogenic MnOx is a highly disordered nanocrystalline phase similar to hexagonal birnessite. This phase is highly reactive and can undergo abiotic transformations or ripening to form phases with higher structural order and less reactivity.

Numerous efforts have been dedicated to understand the structure and reactivity of pure MnOx, yet much still remain unknown regarding the formation, structure, and reactivity of the oxide phases formed biologically and under conditions representative of complex environmental systems. Due to the negative surface charge of MnOx across a wide range of pH, metal cations have strong tendencies to interact with and affect the oxide surface and structure. In order to develop predictive biogeochemical models involving MnOx as the active component, it is critical to develop an in-depth and systematic understanding of the impacts of metal cations on the structure-reactivity relationship of Mn oxides.

Our research systematically investigated the role of common metal cations (e.g. Zn) on the formation, surface, structure, and transforamtion pathways of different types of biotic and abiotic MnOx phases. Zn almost exclusively existed as surface adsorbed species at vacancy sites due to its high structural incompatibility. Its presence significantly altered the morphological and structural properties of the oxides, which resulted in altered sorptive and oxidative reactivities, as well as Mn(II)-induced transformation kinetics and pathways. Such effects were also phase specific, i.e. different MnOx phases show different degrees of alteration. Taken together, our study demonstrated the importance of understanding the structure-reactivity relationship of MnOx under environmetally relevant conditions.